

## Surface composition of NiPd alloys

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Surface segregation in Ni-Pd alloys has been studied using the BFS method for alloys. Not only does the method predict an oscillatory segregation profile but it also indicates that the number of Pd-enriched surface planes can vary as a function of orientation. The segregation profiles were computed as a function of temperature, crystal face, and composition. Pd enrichment of the first layer is observed in (111) and (100) surfaces, and enrichment of the top two layers occurs for (110) surfaces. In all cases, the segregation profile shows oscillations that are actually related to weak ordering tendencies in the bulk. An atom-by-atom analysis was performed to identify the competing mechanisms leading to the observed surface behaviors. Large-scale atomistic simulations were also performed to investigate the temperature dependence of the segregation profiles as well as for analysis of the bulk structures. Finally, the observed surface behaviors are discussed in relation to the bulk phase structure of Ni-Pd alloys, which exhibit a tendency to weakly order.

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# SURFACE COMPOSITION OF Ni-Pd ALLOYS

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## THE BFS METHOD FOR ALLOYS

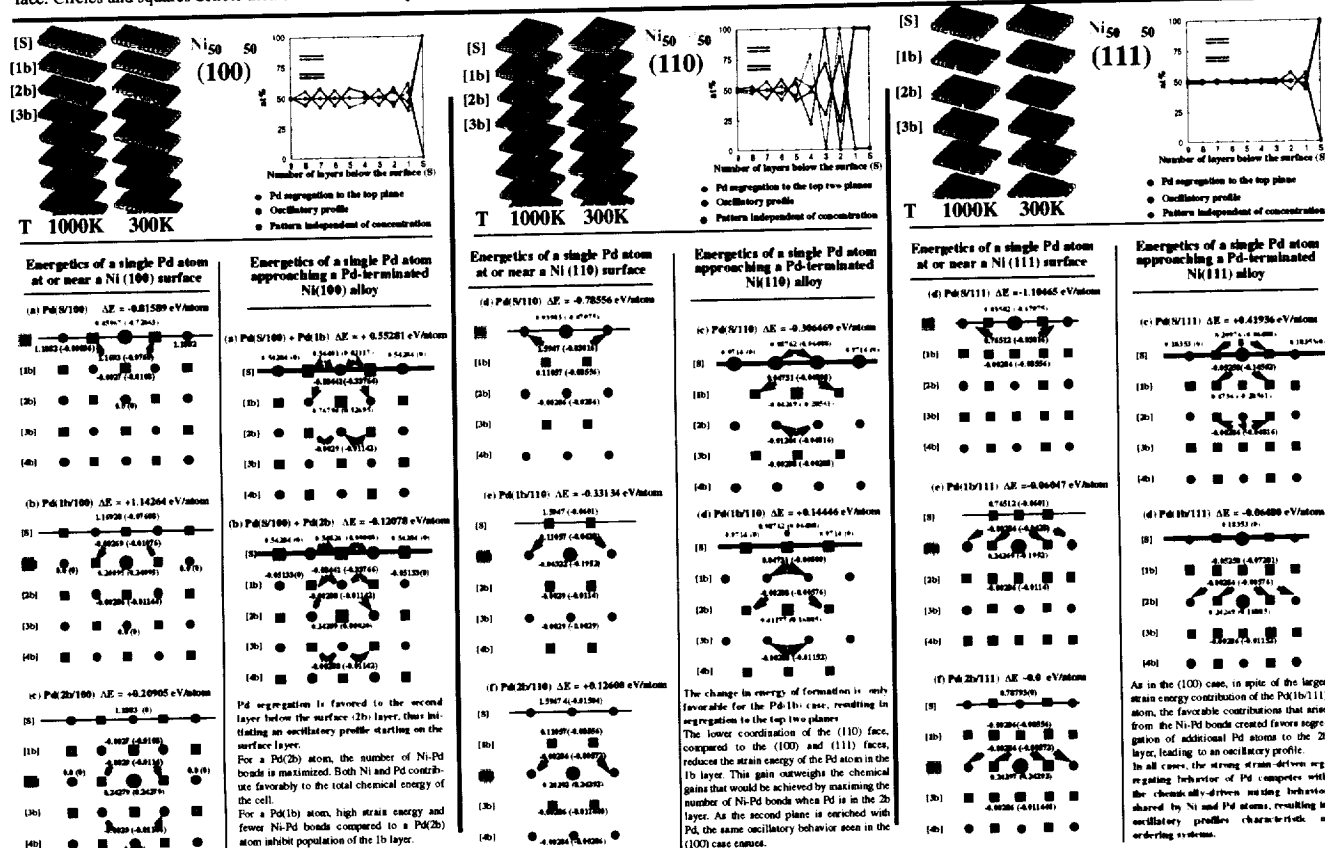
### INTRODUCTION

The most salient features of the surface and bulk behavior in Ni-Pd alloys [1,2] have been studied using the BFS method for alloys. Large-scale atomistic simulations were performed to investigate the segregation profiles computed as a function of temperature, crystal face, and composition. For the low-index surfaces, the method predicts an oscillatory segregation profile. Pd enrichment of the first layer is observed in (111) and (100) surfaces, and enrichment of the top two layers occurs for (110) surfaces. In all cases, the segregation profile shows oscillations that are actually related to weak ordering tendencies in the bulk. An atom-by-atom analysis was performed to identify the competing mechanisms leading to the observed surface behaviors.

- [1] A. Z. Michael et al., Surf. Sci. 416 (1998) 288  
[2] G. N. Derry et al., Surf. Sci. 326 (1995) 59

### MODELING RESULTS

The segregation behavior is explained by an atom-by-atom energetic analysis. The side views, cut perpendicular to the respective surfaces, of Ni cells below (left columns below) show the energy contributions of each equivalent affected atom to the energy of formation of each cell. Also indicated in parenthesis, the total gain or loss in energy of all equivalent atoms with respect to a pure Ni slab. The cell with the lowest value of  $\Delta E$  is favored. The right columns show results for a Ni slab terminated in Pd, with an additional Pd atom near the surface. Circles and squares denote atoms in- and off- the plane of the page, respectively.



Ni-Pd is known to form a solid solution for the whole range of concentrations. However, anomalous physical properties strongly hint at the existence of short range ordering. Experiment [3] also suggests that such ordered regions exist, and that they consist of branched clusters of like atoms in {100}. Within the clusters, like atoms are linked primarily by second nearest neighbors. Monte Carlo simulations using BFS show that such structures form at very low temperatures. As in the surface analysis, the calculations show that the structures observed (the seed of  $L1_2$  ordering), result from the competition between the high strain energy of Pd atoms and the favorable chemical contributions of Ni-Pd bonds.



### CONCLUSIONS

A model was presented for describing surface properties of Ni-Pd alloys that not only reproduces existing experimental results but provides a coherent explanation for what was once a series of apparently conflicting data. It was shown that the competition between strain effects (leading to segregation of Pd to the surface) and chemical effects (leading to oscillations in the profile due to short-range ordering tendencies), must be taken into account to properly describe the top-layer-only Pd enrichment in (100) and (111) Ni-Pd surfaces vs. the two-layer Pd enrichment observed in a (110) termination. These results are consistent with the observed ordering tendencies in bulk Ni-Pd alloys, as suggested by experiment and observed in the theoretical simulations.